"**Synopsis of proposed Ph.D. research work**"

C-C and C-Heteroatom Bond Formations *via* C-H Functionalization

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"Synopsis of proposed Ph.D. research work"

C-C and C-Heteroatom Bond Formations *via* C-H Functionalization

The formation of a Carbon-Carbon and Carbon-Heteroatom bond is a key transformation in organic synthesis and has received widespread interest.[1] Whereas, atom-efficient cross-dehydrogenative coupling (CDC) reactions are considered as the promising methods for new C-C and C-Heteroatom bond formation. The study of novel methods for the construction of a new bonds as such as Carbon-Carbon (C-C), Carbon-Heteroatom (such as C–O, C–N, C-Se *etc.*) *via* direct C-H bond functionalization has thus been attracted a considerable attention in recent years and a significant progress has been achieved.[2] In terms of atom economy,[3] this synthetic method represents one of the most ideal synthetic procedures for selective C-C bond-forming reactions. Compared with traditional cross-coupling reactions, which usually need pre-functionalized starting materials (i.e., Organo-halides and/or Organo-metallic species and thus, lead to stoichiometric amounts of waste), the direct de-hydrogenative functionalization of C (sp^2)-H bond is a more environmentally friendly process.[4] The direct oxidation/oxidative olefination has already attracted much attention because of its chemical versatility and its environmental advantages. Organic chemists have sought to expand the synthetic utility of (hetero)arenes C-H olefination by improving the reactivity and controlling the positional selectivity. We started our study using Imidazo[1,2-*a*]pyridines as a core moiety due to its a number of biologically and pharmaceutically[5] active compounds as well as material science[6].

2. Origin of Research problem:

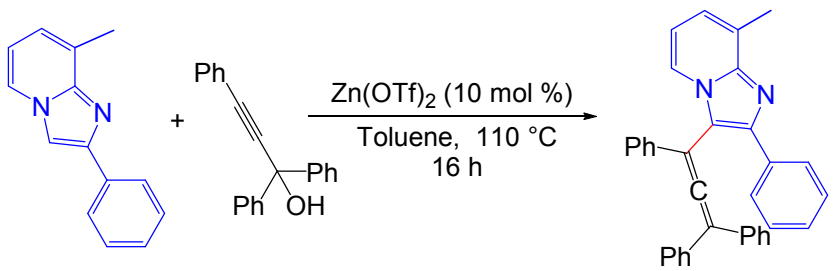
As a consequences C-H functionalization is more time efficient avoiding the multi steps and limitations associated with the preparation of functionalized starting materials and more environmentally friendly as reduces the waste formation. This approach not only streamlines existing syntheses of useful molecular entities, but also contributes to changing the way of chemists thinks about chemical reactivity and plan chemical syntheses. The cross-dehydrogenative coupling reactions of arenes and aromatic heterocycles with alkenes through C-H activation, particularly Pd-catalyzed oxidative cross-coupling namely the Fujiwara-Moritani reaction[7] or the so-called oxidative Heck type reaction have been proven to be the most reliable method in the field of chemical syntheses.[8] The direct oxidation/oxidative olefination has already attracted much attention because of its chemical versatility and its environmental advantages. Recently, many organic chemists have sought to expand the synthetic utility of (hetero)arenes C-H olefination by improving the reactivity and controlling the positional selectivity. Direct and selective replacement of carbon-hydrogen bonds with new bonds (Carbon-Carbon (C-C), Carbon-Heteroatom (such as C–O, C–N, C-Se *etc.*) represents an important and long-standing goal in organic chemistry.

3. Objective(s) of the work:

The formation of a Carbon-Carbon is a key transformation in organic synthesis.[1] The Carbon-Carbon bond formation between of C-3 Substituents 8-methyl-2-phenylimidazo[1,2-*a*]pyridine and 1,1,3-triphenylprop-2-yn-1-ol to prepare tetrasubstituted aromatic allene. Allene is an important functional group in organic chemistry and exhibits distinct reactivity compare to alkene and alkyne. Its structural ability to possess axial chirality differs markedly from other

functional groups. Functionalized allenes are important synthetic targets because of their prevalence in a large number of natural compounds, marketed drugs and optoelectronic materials.[9] These cumulated unsaturated hydrocarbons are indispensable building blocks for a variety of potentially useful carbocycles and heterocycles.[10] In addition, functionalized allenes are the potent precursors of various valuable hydrocarbons.[11] Therefore, the syntheses of allenes having different substituents have drawn much attention of chemists over a long period of time.

Imidazo[1,2-*a*]pyridines are found in a number of biologically and pharmaceutically active compounds.[5] These are also important in the field of material science.[6] So there is a continuous effort for the construction of functionalized imidazo[1,2-*a*]pyridines.[12] The pharmacological activity of imidazopyridine derivatives depends on the nature of substituents at C-3 position. Consequently incorporation of different functionality at C-3 position is of current interest to synthesize diversified derivatives. The literature reveals that there is no such report on the synthesis of 3-allenyl imidazo[1,2-*a*]pyridines. As a part of our ongoing program directed towards the syntheses of diverse imidazopyridine scaffolds[13], herein we wish to disclose a $Zn(OTf)_2$-catalyzed convenient methodology for the synthesis of allene substituted imidazoheterocycles by the coupling between imidazoheterocycles and 1,1,3-triphenylprop-2-yn-1-ol.



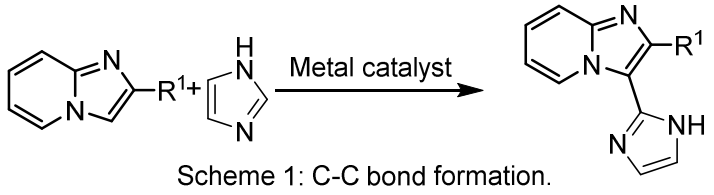
4. Methodology:

Toluene (1.5 mL) was added to a mixture of 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (42 mg, 0.20 mmol) and 1,1,3-triphenylprop-2-yn-1-ol (57 mg, 0.20 mmol) in the presence of 10 mol % $Zn(OTf)_2$ (7.3 mg, 0.02 mmol) at 110 °C for 16 h in a reaction tube. After completion of the reaction (monitored by TLC) it was allowed to cool at room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent under reduced pressure and finally it was purified by column chromatography on silica gel (60-120 mesh) using petroleum ether:ethylacetate = 19:1 as an eluent to afford the pure product. The structure was determined on the basis of ^{13}C NMR spectra where allene (sp-C) was observed at 209.9 ppm and structure of the product was confirmed by the single crystal X-ray analysis.[14]

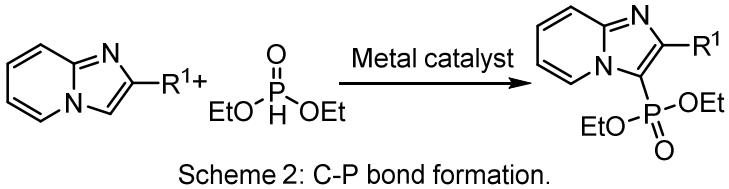
Instruments used:

- lab instruments like column chromatography, rotary evaporator *etc*
- FT-NMR instrument (BRUKER AVANCE 400 MHz).
- FT-IR (SHIMADZU 8400S)
- XRD (BRUKER).

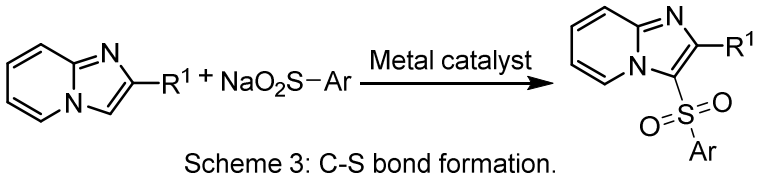
5. Future Prospect:



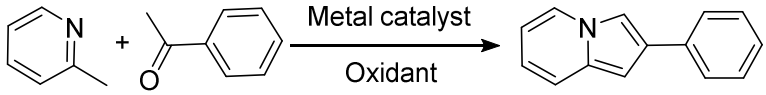
Scheme 1: C-C bond formation.



Scheme 2: C-P bond formation.



Scheme 3: C-S bond formation.



Scheme 4: C-C and C-N bond formation

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